JAPANESE [JP,11-222402,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to an antibacterial resin composition useful as a coating agent etc. including an antimicrobial polymer particle which reveals antibacterial properties effectively to various microorganisms, such as bacteria and mold, and a manufacturing method for the same, and said antimicrobial polymer particle.
[0002]
[Description of the Prior Art]In recent years, the antibacterial treatment is considered by various products. This antibacterial treatment is performed by the method of kneading an organic system or an inorganic system antimicrobial agent to a plastic, or usually coating the paint containing an antimicrobial agent, etc. The organic system antimicrobial agent is excellent in antibacterial properties, an instantaneous effect, and the dispersibility over resin among said antimicrobial agents. However, there is a problem of a bacillus besides the elution from a substrate, heat resistance, and the safety to a human body revealing drug tolerance. On the other

hand, the inorganic system antimicrobial agent which made the inorganic carrier (particle state inorganic carriers, such as zeolite and silica gel) support the metal ions (silver, zinc, copper, etc.) which have antimicrobial activity, It excels in the safety to the human body which various advantages, for example, heat resistance, a large antimicrobial spectrum, and drug tolerance cannot gain easily, etc., and an antimicrobial agent is in use now. As for the antimicrobial activity of an antimicrobial agent, since it is revealed on the surface of the product which carried out the antibacterial treatment, in order to use an antimicrobial agent efficiently, it is effective to coat an antimicrobial agent on the surface of a product.

[0003]However, if an inorganic system antimicrobial agent is applied to coating of a base material surface, various problems will arise. For example, in order that an inorganic system antimicrobial agent may make the zeolite of hydrophilic nature, silica gel, etc. a carrier fundamentally, Since it is difficult to distribute i antimicrobial agent uniformly to a coating agent and the diameter of ii carrier particles and specific gravity are comparatively large, when it blends with a coating agent, It sediments in a coating agent and is easy to dissociate, and in order to raise contact frequency with a bacillus and to make sufficient antibacterial effect reveal, it is necessary to blend a lot of antimicrobial agents. Since compatibility with an iii organic binder and adhesion are inferior, while an antimicrobial agent is easily omitted from the coating film surface, the mechanical strength of a coating film also falls and the transparency of iv coating film is also spoiled. Depending on the kind of inorganic system antimicrobial agent, the exposure of beams of light, such as ultraviolet rays, may color.

[0004]On the other hand, the antimicrobial agent which made the silver ion hold to an organic high polymer is also proposed. The deodorization antibacterial-properties constituent containing the solution or the dispersion liquid, and the silver ion of a carboxyl group containing polymer is indicated by JP,2-288804,A. The antimicrobial agent which made the surface of acrylic polymer particles support a silver ion is indicated in the sulfonic group by JP,4-173712,A. The antimicrobial agent which comprised an acrylic ester (meta) (meta) acrylic acid-silver polymer particle is indicated by a maleic acid polymer, the antimicrobial polymer which comprised combination of the silver ion, and JP,8-165212,A at JP,8-151310,A. However, in these antimicrobial agents, a silver ion is eluted at an early stage, it continues at a long period of time, and high antibacterial properties cannot be maintained. Antimicrobial activity cannot be revealed effectively and the bottom of the high humidity environment these days and a microorganism are especially apt to increase, and place-equipped-

with-a-water-supply environment is not enough for durability.
[0005]
[Problem(s) to be Solved by the Invention]Therefore, in spite of using the antibacterial metallic component of an inorganic system for the purpose of this invention, there is in providing the antibacterial resin compositions containing the antimicrobial polymer particle which continues at a long period of time and can reveal high antimicrobial activity effectively, and its antimicrobial polymer particle, and those manufacturing methods. Other purposes of this invention can reveal antibacterial properties effectively with the increase in humidity or moisture, and there are in providing the antibacterial resin compositions containing the antimicrobial polymer particle provided with environmental response nature, and its antimicrobial polymer particle, and those manufacturing methods. Even if it uses the purpose of further others of this invention as resin compositions, such as a coating agent, there is in providing the antibacterial resin compositions containing the antimicrobial polymer particle and it which are excellent in dispersibility, compatibility with an organic high polymer, and a coating characteristic, and those manufacturing methods.
[0006]
[Means for Solving the Problem]If this invention persons make a carrier of an organic high polymer which has hydrophilic units support an antibacterial metallic component wholeheartedly as a result of examination in order to solve said technical problem, An antibacterial metallic component could be emitted according to humidity environment, it found out that it continues at a long period of time, and high antimicrobial activity can be maintained, and that an antibacterial resin composition with it was obtained, and this invention was completed. [high compatibility with an organic high polymer and] [useful as an antimicrobial coating agent etc.] That is, an antibacterial metallic component which comprised a metal ion or metallic compounds combines with a polymer particle chemically, and an antimicrobial polymer particle of this invention is supported. In this antimicrobial polymer particle, an antibacterial metallic component is chemically combined with a polymer particle via a functional group which usually contains an oxygen atom, a nitrogen atom, and at least one atom chosen from a group which consists of sulfur atoms. Namely, a polymer particle which constitutes antimicrobial polymer, It comprises hydrophilic polymer which has the structure of cross linkage containing hydrophilic units, a unit which has a combinable functional group chemically to an antibacterial metallic component including at least one atom chosen from an oxygen atom, a nitrogen atom, and a sulfur atom, and a bridge construction unit. Mean

particle diameter of a polymer particle may be 0.1 nm - about 100 micrometers. As said antibacterial metallic component, silver, platinum, copper, zinc, nickel, cobalt, molybdenum, chromium, etc. can be illustrated. A holding amount of an antibacterial metallic component is metal conversion, and is about 0.01 to 70% of the weight of the whole. Said antimicrobial polymer can be manufactured by joining together chemically and making a functional group of hydrophilic polymer particles which have the structure of cross linkage support an antibacterial metallic component which comprised a metal ion or metallic compounds. A resin composition of this invention contains said antimicrobial polymer particle and resin (binder resin etc.), and they can be used for it as an antibacterial coating resin composition etc. This antibacterial resin composition can be prepared by mixing said antimicrobial polymer particle and resin (binder resin etc.).
[0007]"Support" of an antibacterial metallic component as used herein means that an antibacterial metallic component is held the surface and/or inside a polymer particle, as long as antibacterial properties are revealed. It may use for a meaning including both sides of an ionic bond and a coordinate bond with a "chemical bond" and "chemical bonds", and may only be called "coordination." "Hydrophilic polymer not constructing a bridge" and "hydrophilic polymer which has the structure of cross linkage" may only be named "hydrophilic polymer" generically.
[0008]
[Embodiment of the Invention][Hydrophilic polymer particles] The polymer particle comprises hydrophilic polymer which has a functional group which an antibacterial metallic component can configurate, and may be any of synthetic macromolecule and naturally-ocurring polymers. Hydrophilic polymer particles have the structure of cross linkage, and are usually poor solubility or insolubility to a solvent. The hydrophilic polymer particles which function as a carrier contain at least one atom chosen from hydrophilic units, an oxygen atom and a nitrogen atom, and the sulfur atom, And it comprises a ligating property unit which has a combinable functional group (especially ligating property group) chemically to an antibacterial metallic component, and a bridge construction unit. In hydrophilic polymer particles, hydrophilic units and the ligating property unit which has a functional group may be of the same kind, or may differ from each other.
[0009]Various hydrophilic fragmentation and segments can be used as hydrophilic units, For example, By hydrolysis of carboxyl group content unit [(meta) unit formed by carboxyl group or acid anhydride group content monomers, such as acrylic acid and maleic anhydride,] hydroxyl content unit [vinyl acetate. Unit] formed by hydroxyl content monomers to generate, such as a vinyl alcohol

unit and hydroxy C_{2-3} alkyl (meta) acrylate, Ether group content unit [vinyl C_{1-4} alkyl ether, Unit] in which polyethylene-glycol mono- ** was formed by ether group content monomers, such as di (meth)acrylate and a polyethylene glycol, A nitrogen content unit [unit formed by nitrogen content monomers, such as vinyl pyrrolidone, vinylpyridine, acrylamide (meta), methylol(meta) acrylamide, and N,N-dialkylamino alkyl (meta) acrylate,] etc. can be illustrated. Hydrophilic polymer may have several different hydrophilic units, and hydrophilic units may form a salt as occasion demands.

[0010]They are contained in desirable hydrophilic units by the hydrophilic units which form water-soluble polymer and have compatibility to hydrophobic resin, and as such hydrophilic units, The unit (for example, hydrophilic units formed with acrylamide (meta), N-substitution (meta) acrylamide, etc.) containing a nitrogen atom (especially an amide group or N-substituted amide group) can be illustrated. As N-substitution (meta) acrylamide, for example N-C_{1-6} alkyl (meta) acrylamide, such as N-methyl(meta) acrylamide, N-ethyl(meta) acrylamide, and N-butyl(meta) acrylamide, N-C_{1-6} acyl (meta) acrylamide etc. can be illustrated. If hydrophilic units are formed with N-C_{1-6} alkyl (meta) acrylamide, such as N-butylacrylamide, it can give temperature sensitive to a polymer particle.

[0011]In a ligating property unit, as a functional group (especially ligating property group) containing an oxygen atom, For example, a carboxyl group or its derivative group (an acid halide group, an acid anhydride group, etc.), Hydroxyl, an acyl group (C_{1-4} acyl groups, such as formyl and an acetyl group etc.), A carbonyl group, a poly carbonyl group including acetylacetone structure, an ether group, A crown ether group, aromatic polyhydroxyl including catechol structure, an aromatic hydroxy carbonyl group including salicylic acid structure, a polycarboxylic acid group including phthalate structure, an epoxy group, oxygen content heterocycle groups (a furil group, a chromanyl group, etc.), etc. can be illustrated.

[0012]As a functional group (especially ligating property group) containing a nitrogen atom, An amino group and mono- ** For example, a dialkylamino group (a mono- C_{1-4} alkylamino group, a JI C_{1-4} alkylamino group, etc.), azo, an amidino group, a hydrazino group, a hydrazono group, a cyano group, and a nitrogen content heterocycle group (a pyrrolyl group and an imidazolyl group.) Azacrown ether groups, such as a pyridyl group, a bipyridyl group, a pyrrolyl group, a piperidinyl group, a piperazinyl group, a

quinolyl group, a benzimidazolyl group, and a phenan SURORIRU group, etc. can be illustrated. As a nitrogen content functional group, an amino group and an imino group may be used in many cases, and nitrogen content functional groups may be heterocycle groups, such as a pyridyl group.

[0013]As a functional group (especially ligating property group) containing a sulfur atom, A sulfhydryl group (thiol group), a thioxo group, a thienyl group, a thioacetyl group, An alkyl thionyl group, a thiocarbamoyl group, a sulfonyl group, a thiocarboxyl group, A sulfonic group (sulfonic group), a sulfinic acid group (sulfino group), a thiourea group (thio ureido group), a thia crown ether group, a thioether group, heterocycle groups (thiophenyl group etc.), etc. can be illustrated.

[0014]Hydrophilic polymer particles may have a functional group containing the functional group which has two or more atoms chosen from an oxygen atom, a nitrogen atom, a sulfur atom, etc., for example, an oxygen atom, and a nitrogen atom. As such a functional group, an amino alcohol group like a nitro group, an ureido group, and an amino hydroxyethyl group for example, An aminophenol group, a KINORINO group, an amino-polycarboxylic-acid group like an IMIJINO acetic acid group, an oxime group, an amide oxime group, heterocycle groups (a morpholino group, a morpholinyl group, etc.), etc. can be illustrated.

[0015]Two or more above-mentioned functional groups are combinable. Since the strength of combination with a metal ion or metallic compounds changes with kinds of functional group, discharge of the antibacterial metallic component from hydrophilic polymer particles is controllable by using combining the functional group from which a kind differs two or more.

[0016]The kind of functional group can be chosen according to the kind of antibacterial metallic component. An oxygen content functional group [for example, carboxyl group] etc., a nitrogen content functional group [for example, nitrogen content heterocycle groups (imidazolyl group, pyridyl group, bipyridyl group, etc.) etc.], and a sulfur content functional group [thiol group, thio ureido group], etc. are contained in a desirable functional group. If such a functional group and an antibacterial metallic component (for example, silver ingredient) are combined, a complex can be formed effectively.

[0017]The bridge construction unit for introducing the structure of cross linkage into hydrophilic polymer particles may be constituted from a condensation nature group or fragmentation like self-crosslinked polymer particles (for example, hardening or a cross linked particle of thermosetting resin, etc.), and may consist of cross linking agents. Like [heat resistance of a crosslinked polymer particle is high, and] a baking coating, even if exposed to an

elevated temperature (for example, about 300 **), high tolerance is shown. As a cross linking agent which constitutes a bridge construction unit, a polymerization nature unsaturated monomer by the polymer (vinyl polymerization type polymer) used as a raw material. Usually, polyfunctional polymerization nature monomer [divinylbenzene, methylenebis (meta) acrylamide, Ethylene glycol di(metha)acrylate, diethylene GURIKORUJI (meta) acrylate,], such as propyleneglycol di(meth) acrylate, dipropylene GURIKORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, penta ERIS RITORUTORI, or tetra (meta) acrylate, is used.

[0018]In the hydrophilic polymer (a condensed type or addition condensation type polymer) which uses condensation or an addition reaction nature monomer as a raw material, the compound which has two or more reactive functional groups to the functional group of polymer can be used as a cross linking agent. When hydrophilic polymer has two or more carboxyl groups or acid anhydride groups, as a cross linking agent, For example, the epoxy compound which has an epoxy group of polyvalent-metal-ion (magnesium ion, Al ion, zirconium ion, etc.); polyisocyanate; polyamine; plurality; a screw oxazoline compound etc. are mentioned. When hydrophilic polymer has hydroxyl, as a cross linking agent. for example, polyisocyanate; polyvalent carboxylic acid or its reactive derivative (acid halide.) acid anhydride; -- the compound (dichlorodimethylsilane.) which has a hydrolytic silyl group The compound which has the methylol group or alkoxy methyl groups of; plurality, such as dichloro tetramethyl disiloxane, methyl trimetoxysilane, and methyl triethoxysilane (urea resin, melamine resin, etc.); a screw oxazoline compound etc. are mentioned. The epoxy compound which has an epoxy group of compound; plurality which has polyisocyanate; polyvalent carboxylic acid or its reactive derivative; hydrolytic silyl group, for example when hydrophilic polymer has an amino group, an amide group, etc.; a screw oxazoline compound etc. can use it as a cross linking agent.

[0019]The degree of cross linking of hydrophilic polymer particles is bridge construction unit (or cross linking agent) conversion, and is about 1 to 10 % of the weight more preferably 0.5 to 20% of the weight 0.1 to 30% of the weight, for example.

[0020]Said ligating property unit (for example, unit formed by the monomer containing nitrogen content groups, such as said carboxyl group and a nitrogen content heterocycle group, a sulfhydryl group, etc.) which has ** hydrophilic nature to the hydrophilic polymer particles which have the structure of cross linkage, A copolymer or a co-condensation product with a bridge construction unit (for example, unit formed by cross-linking monomers and cross linking agents, such as a polyfunctional polymerization nature monomer),

** Said hydrophilic units (meta) (unit formed by monomers, such as acrylamide and N-substitution (meta) acrylamide), The copolymer or co-condensation product of said ligating property unit (for example, unit formed by the monomer containing said carboxyl group, a nitrogen content functional group, a sulfhydryl group, etc.) and a bridge construction unit (for example, unit formed by a polyfunctional polymerization nature monomer etc.) is contained.

[0021]Further these hydrophilic polymer particles as a copolymerization unit. For example, vinyl ester system monomers, such as aromatic vinyl monomers, such as acrylic system monomers (meta), such as acrylic acid alkyl ester (meta) and acrylonitrile (meta), and styrene, and vinyl acetate, The unit formed by olefins, such as containing halogen monomers, such as polyvinyl chloride and a polyvinylidene chloride, ethylene, and propylene, etc. may be included, and as long as it is required, it may denaturalize further.

[0022]The cross linked polymer in which desirable hydrophilic polymer particles have hydrophilic polymer gel [, for example, a ligating property unit, (bridge construction polyacrylic acid, bridge construction polyvinyl pyridine, etc.), An acrylamide unit and a ligating property unit. Cross linked polymer which it has (the structure of cross linkage.) The acrylamide which it has. (Meta) It can constitute from], such as an acrylic acid copolymer, an acrylamide vinylpyridine copolymer which has the structure of cross linkage, an acrylamide mercaptomethyl substitution styrene copolymer which has the structure of cross linkage, and an acrylamide (meta) acrylic acid-vinylpyridine copolymer which has the structure of cross linkage.

[0023]The concentration of the functional group (ligating property unit) of hydrophilic polymer particles can be chosen according to the holding amount of an antibacterial metallic component, for example, is about 0.1-5 millimols preferably 0.01 to 10 millimol per 1g of polymer particles. The amount used which is a monomer which has a ligating property unit can be chosen from about 25 to 100% of the weight of the range preferably [it is desirable and] to 10 to 100 % of the weight, and a pan five to 100% of the weight, for example.

[0024]In order to make the antimicrobial activity of an antibacterial metallic component reveal effectively, hydrophilic polymer particles may be porosity. the specific surface area of porosity particles -- 10-1000m^2/g -- desirable -- 50-1000m^2/g -- it is a 100-1000 m^2/g grade still more preferably.

[0025]The shape of particle state hydrophilic polymer may be any, such as a globular shape, tabular, rod form, and petaloid. It may be dryness, for example, 0.1 nm - 100 micrometers, preferably, the

mean particle diameter of hydrophilic polymer particles may be 5 nm - a 10-micrometer (especially 10-nm - 1 micrometer) grade more preferably, and may be about 10-500 nm 1 nm - 30 micrometers (for example, 1 nm - 5 micrometers). Although it can choose according to a use, if the polymer particle of nano size is used, the particle diameter of hydrophilic polymer particles can raise the content of the antibacterial metallic component in the dispersibility in a resin composition, and a resin composition, and can reveal high antibacterial properties with a small addition. The carrying state of the antibacterial metallic component to hydrophilic polymer particles (for example, by copolymerization etc.) The introduction to the polymer particle of several functional groups from which the ligating property to an antibacterial metallic component differs, etc., By controlling the grade (for example, [of a polymer particle / the hygroscopicity or swelling]) of mixing of two or more polymer particles which have a different functional group, and the hydrophilic nature of a polymer particle, according to ambient environment humidity etc., discharge of an antibacterial metallic component can be controlled and the antimicrobial agent of quick action thru/or durability can be obtained.

[0026][Antibacterial metallic component] To hydrophilic polymer particles, an antibacterial metallic component carries out a chemical bond, and is supported. In particular, the chemical bond of the antibacterial metallic component is carried out to hydrophilic polymer particles via said functional group (functional group containing an oxygen atom, a nitrogen atom, a sulfur atom, a phosphorus atom, etc.). These antibacterial metallic components are independent, or an antibacterial metallic component can be constituted from the metal ion and metallic compounds which have antibacterial properties, and they can be used, combining them two or more sorts. As a metal ion which has antibacterial properties, a silver ion (silver (I) or (II) ion), platinum ion, a copper ion, zinc ion, nickel ion, cobalt ion, molybdenum ions, and chromium ions can be mentioned, for example. Desirable antibacterial metal ion is silver (I) ion, a copper ion and zinc ion, especially a silver ion.

[0027]As metallic compounds which have antibacterial properties, at least a kind of metallic compounds chosen from silver, platinum, copper, zinc, nickel, cobalt, molybdenum, and chromium can be illustrated, and the metallic compounds of reactivity or ligating property can usually be used to the functional group of said polymer. Said metallic compounds may be metal complexes and this metal complex may be anionic and cationic or neutral any. As for an opposite cation, in the case of an anionic complex, it is preferred that it is quaternary ammonium (phenyldimethyl alkylammonium, didecyl dimethylannmonium, Sept Iles trimethylammonium, tetramethylammonium, etc.) which has

antibacterial properties.
[0028]In desirable metallic compounds, a silver compound (AgCl, AgBr, etc.), for example, a silver halide, A halogen acid salt and a fault halogen acid salt ($AgClO_4$, $AgClO_3$, $AgBrO_3$, $AgIO_3$, etc.),

Inorganic acid salts (silver sulfate, silver nitrate, silver carbonate, etc.), organic acid salt (silver acetate, oxalic acid silver, etc.), and complexes (a dicyano complex, a JICHIOSURU fight complex, a diammine complex, a dichloro complex, etc.) are contained. Said antibacterial metallic components (silver ingredient etc.) are configurated to the functional group of said polymer, and may form complexes (a thiol complex, a thio ureido complex, a pyridyl complex, a bipyridyl complex, a phenan TORORIRU complex, a histidyl complex, etc.). If the antibacterial metallic component which can be configurated is used to the functional group of polymer, the content of an antibacterial metallic component can be increased, it continues at a long period of time, and antimicrobial activity can be maintained. Even if antimicrobial activity falls, it is easily renewable by being immersed in the solution containing antibacterial metal ion.
[0029]The holding amount of an antibacterial metallic component should just be a range which does not spoil antibacterial properties, for example, is metal conversion, and the full weight of hydrophilic polymer particles is preferred 0.01 to 70% of the weight, and it is about 5 to 40 % of the weight one to 40% of the weight especially more preferably 0.1 to 50% of the weight.
[0030]In the desirable antimicrobial agent of this invention, for example Nitrogen content hydrophilic units, Ligating property units, such as an oxygen content functional group, a nitrogen content functional group, and a sulfur content functional group, The hydrophilic polymer particle with a mean particle diameter of 1 nm - 10 micrometers (for example, 1 nm - 3 micrometers, preferably 10-500 nm, especially about 50-500 nm) which have a bridge construction unit, It comprises an antibacterial silver ingredient supported by carrying out a chemical bond (especially coordinate bond) to said functional group of this polymer particle. In this antimicrobial agent, the holding amount of an antibacterial silver ingredient is silver conversion, and is a 1 to 50% of the weight of whole (preferably 5 to 40 % of the weight) grade. Hydrophilic polymer particles may contain the organic system antimicrobial agent further as occasion demands in order to improve antimicrobial activity.
[0031][Manufacturing method of an antimicrobial polymer particle] The antimicrobial agent of this invention can be prepared by joining together chemically and making the functional group of hydrophilic polymer particles support an antibacterial metallic component. Said hydrophilic polymer particle can be prepared

using the method of common use of grinding and classification, suspension polymerization, an emulsion polymerization, etc. As the typical method of preparation of bridge construction hydrophilic polymer particles, The method of polymerizing the monomeric mixture which comprised a monomer corresponding to a ligating property unit, a monomer corresponding to hydrophilic units, and a cross linking agent for forming the structure of cross linkage can be illustrated using a polymerization initiator among the precipitate polymerizing method (it is a mixed solvent of water and a hydrophilic solvent especially), for example, a nonaqueous solvent. The particle diameter of hydrophilic polymer particles can be controlled and the hydrophilic polymer particles which have the particle diameter of a nano order can be made to generate efficiently by adjusting the kind of hydrophilic solvent, and the rate of water and a hydrophilic solvent in this method. As a hydrophilic solvent, ether, such as ketone, such as alcohols, such as methanol, ethanol, isopropanol, and butanol, and acetone, dioxane, and a tetrahydrofuran, and these mixed solvents can be illustrated. the rate of water and a hydrophilic solvent -- former/latter =1 / 99 - 70/30 (% of the weight) -- it can choose suitably [it is desirable and] from the range of 50/[3/97 -] 50 (% of the weight) grade. Especially in this precipitate polymerizing method, while being able to control the generated grain size, without using dispersion stabilizer, washing and recovery of particles are easy and hydrophilic polymer particles can be obtained by low cost.

[0032]Bridge construction hydrophilic polymer particles the solution of hydrophilic polymer containing the functional group which can configurate an antibacterial metallic component, How to add and harden a cross linking agent after carrying out addition mixing at a poor solvent and making a polymer particle generate in a medium, After carrying out addition mixing of the mixed liquor of a cross linking agent and hydrophilic polymer at the poor solvent to polymer and making a polymer particle generate in a medium, it can obtain by the method of hardening, the spray-drying method which carries out spray drying of the mixture of a cross linking agent and hydrophilic polymer, etc. The bridge construction hydrophilic polymer particles of the thermosetting resin which has self crosslinkability can be prepared like the above, without using a cross linking agent.

[0033]An antibacterial metallic component may originate in said monomer and cross linking agent used as the raw material of polymer, and may introduce the functional group in which a chemical bond is possible into the generated polymer using a polymeric reaction etc. As a method of introducing said functional group into polymer using a polymeric reaction, the method of common use according to the preparing method of metal ion

adsorbent resin, such as chelating resin, is employable, for example. For example, a sulfhydryl group and a bipyridyl group can be introduced according to Ueyama, N, et al. Inorg. Chem. Acta. 89, and the method indicated to 19-23 (1984). Introduction of an imidazole group can be performed by for example making histidine react to the polymer which has a chloromethyl group.
[0034]Support of the antibacterial metallic component to a polymer particle can be performed by swelling a polymer particle with a solvent as occasion demands, carrying out addition mixing of the solution containing an antibacterial metallic component for example, and carrying out the chemical bond of the antibacterial metallic component to polymer. After making an antibacterial metallic component support, polymer is washed and the antimicrobial polymer particle of this invention is obtained by drying.
[0035]Since an antibacterial metallic component and hydrophilic polymer particles are carrying out the chemical bond of the antimicrobial polymer particle of this invention, it continues at a long period of time, and it reveals high antimicrobial activity. Since it comprises hydrophilic polymer especially, under the high humidity environment in which these days and a microorganism breed easily, it absorbed water, particles swelled, and it becomes easy to emit the antibacterial metallic component inside particles, and has environmental response nature. In particular, in particles (for example, particles of nano size), distance until the antibacterial metallic component inside particles reaches a particle surface is short, and, moreover, can improve the contacting efficiency of an antibacterial metallic component, and bacteria and a microorganism according to increase of a particle surface product. It is also possible for the hydrophilic polymer particles to which antimicrobial activity fell to only be immersed in the solution (solution) containing an antibacterial metallic component, and to reproduce. An antibacterial metallic component can be supported stably, and even if it irradiates with ultraviolet rays etc., it does not discolor. And since a carrier is an organic high polymer, it is possible to form an antibacterial coating film with the dispersibility of a polymer particle for hydrophobicity and the compatibility to the both sides of a hydrophilic organic high polymer to be high, and high and high transparency. Therefore, antimicrobial polymer of this invention is useful although an antibacterial resin composition is constituted combining resin (for example, resin used for an ultraviolet curing nature paint or distemper).
[0036][Antibacterial resin composition] In an antibacterial resin composition, resin can be chosen from the wide range according to a use. as resin -- thermoplastics [olefin system resin (polyethylene and polypropylene.) Polyethylene, denaturation polypropylene, etc.

which denaturalized by carboxyl group, acid anhydride group, an epoxy group, etc., Acrylic resin (poly methyl methacrylate, carboxyl containing acrylic resin, a hydroxyl content acrylic resin, epoxy group containing acrylic resin, etc.), Styrene resin (copolymer of polystyrene, an AS resin, ABS plastics, styrene, and an acrylic (meta) monomer, etc.), Vinyl acetate system resin (polyvinyl acetate, an ethylene-vinylacetate copolymer, a vinyl acetate vinyl chloride copolymer, etc.), A vinyl alcohol system polymer (polyvinyl alcohol, ethylene-vinylalcohol copolymer, etc.), VCM/PVC system resin (polyvinyl chloride etc.) and polyester resin (polyalkylene terephthalate and polyalkylene naphthalate.)], such as polyurethane resin, such as copolymerized polyester resin and modified polyester resin, polyamide resin, and rubber, a thermosetting resin [epoxy resin, phenol resin, urethane resin, unsaturated polyester resin, vinyl ester resin, diallyl phthalate resin, silicone resin,] and photo-setting resin [epoxy (meta) acrylate, [, such as amino resin (urea resin, melamine resin, etc.)] Photoresist monomer [, such as photoresist oligomer, such as urethane (meta) acrylate and polyester (meta) acrylate, polyfunctional (meta) acrylate, and a nitrogen content monomer,]] etc. can be illustrated. These resin is independent, or it can be used, combining it two or more sorts. Resin may be water soluble resin and organic solvent soluble resin. Resin can be used as aqueous dispersion and non-aqueous dispersing elements (an emulsion, latex, etc.) (organosol etc.).

[0037]The antibacterial molding resin composition containing the molding resin in which the resin composition of this invention is used for molding processes, such as extrusion molding and injection molding, Although it is good in ********** containing resin for adhesives, it is preferred that it is a resin composition for coating containing resin for coating agents (binder resin), such as a paint. If the coat (coating film) containing an antimicrobial polymer particle is formed, on the surface of a product, it continues at a long period of time, and high antimicrobial activity can be maintained effectively. The gestalten of the resin composition for coating may be any, such as non-solvent type coating agents, such as a granular material coating agent which comprised a particulate matter, an aqueous coating agent by which the solvent was constituted from an aqueous solvent, a solvent type coating agent by which the solvent was constituted from an organic solvent, and an ultraviolet curing type paint. The amount of the antimicrobial polymer particle used can be chosen from the wide range, for example, is solid content conversion, and is about 0.5-50 weight sections still more preferably 0.1 to 100 weight section preferably 0.01 to 200 weight section to resin 100 weight section. 1-500 micrometers of thickness of a coat (antibacterial layer) can be chosen suitably [it is desirable

and] from the range of about 5-300 micrometers, for example.
[0038]The antibacterial resin composition of this invention may contain various additive agents (an antioxidant, an ultraviolet ray absorbent, a thermostabilizer, etc.), for example, stabilizer, a plasticizer, a spray for preventing static electricity, fire retardant, a dispersing agent, a surface-active agent, a bulking agent, colorant, a viscosity controlling agent, an antiseptic, an antifungal agent, a RE ** ring agent, etc.
[0039]An antibacterial resin composition (or resin composition for coating) can be prepared by mixing a solvent, an additive agent, etc. with said antimicrobial polymer particle, and resin or binder resin as occasion demands. If the gestalt of a resin composition is embraced, and and common use asks, a kneading machine, a dispersion machine, a mixer, etc. can be used for preparation of a resin composition.
[0040]A coat can be formed by optical applying the resin composition for coating to a substrate, and drying or (it is heat cure by necessity) glaring with a conventional coating method (UV irradiation etc.). As a substrate, ceramics, metal, etc. containing paper, wood, a plastic, and glass can be used.
[0041]If the antimicrobial polymer particle (antimicrobial agent) of this invention is used for coating agents, such as a paint, an antimicrobial agent can be distributed uniformly and easily, dispersion stability is high, and sedimentation etc. can be prevented from arising. Therefore, even if it is a little antimicrobial agents, the activity of an antimicrobial agent can be revealed effectively. Since compatibility and adhesion with an organic binder are high, a coating film with a mechanical strength it is uniform and high and high transparency can be formed.
[0042]
[Effect of the Invention]Since the antibacterial metallic component of the antimicrobial agent is carrying out the chemical bond to the hydrophilic polymer particles which have the structure of cross linkage in this invention, in spite of using the antibacterial metallic component of an inorganic system, it continues at effective and a long period of time, high antimicrobial activity can be revealed, and durability is high. Since a polymer particle is hydrophilic nature, antibacterial properties could be effectively revealed with the increase in humidity or moisture, and it has environmental response nature. Even if it uses as resin compositions, such as a coating agent, an antimicrobial agent is excellent in dispersibility, compatibility with an organic high polymer, and a coating characteristic.
[0043]
[Example]This invention is not limited by these examples although this invention is explained more below at details based on an

example.
Example 1 [preparation of bridge construction hydrophilic polymer particles] acrylamide 4g (0.056-mol and 72.2-mol %), The methylenebis acrylamide 2.4g (0.0156-mol and 20.1-mol %), And the mixed liquor of 1.6 g (0.006-mol and 7.7-mol %) of 4-(N,N-diethyl dithiocarbamate) styrene, It added to 86 ml of ethanol, and the mixed solvent of 6 ml of water, and the precipitate polymerization was carried out at the temperature of 60 ** among argon atmosphere for 17 hours using 0.05 g of azobisisobutyronitrile. In this reaction, after heating in temperature of 60 **, after about 2.5-hour progress, the polymerization system became cloudy and the polymer particle generated.
[0044][Hydrolysis] 100 ml of ethanol, 50 ml of water, and the mixed liquor of 2 g of sodium hydroxide were added, among argon atmosphere, after agitating into reaction mixed liquor for 5 hours and hydrolyzing into it at the temperature of 70 **, it centrifuged into it and 100 ml of ethanol and the mixed solvent of 100 ml of water washed precipitate particles twice into it. In order to make a sulfhydryl group generate, precipitate particles were added in water, 1N-chloride was added, and pH was adjusted to about 5, and it agitated one whole day and night, and hydrolyzed. Subsequently, mixed liquor was centrifuged, 100 ml of ethanol and the mixed solvent of 100 ml of water washed precipitate particles 3 times, and 150 ml of water washed twice further.
[0045]Particles were colored thin orange, when the mixed liquor of the silver nitrate 1.05g (0.006 mol) and 150 ml of water was added to the precipitate particles which [silver complex support polymer particle prepared] washed and it agitated at the room temperature to them for 2 hours. By centrifuging mixed liquor, washing precipitate particles twice and carrying out reduced pressure drying with 150 ml of methanol, once, with 150 ml of water, The silver complex support polymer particle (mean particle diameter of about 60-90 nm) was obtained (the yield of 7.8 g (dry solid conversion), 14.9 % of the weight of moisture contents, 22.8 % of the weight of silver content, 89.9% of yield).
[0046]Example 2 [preparation of bridge construction hydrophilic polymer particles] acrylamide 4g (0.056 mol), The methylenebis acrylamide 2.4g (0.0156 mol) and the mixed liquor of 1.6 g (0.0152 mol) of 4-vinylpyridine, It added to 86 ml of ethanol, and the mixed solvent of 6 ml of water, and the precipitate polymerization was carried out at the temperature of 60 ** among argon atmosphere for 17 hours using 0.05 g of azobisisobutyronitrile. In this reaction, after heating in temperature of 60 **, after about 1.5-hour progress, the polymerization system became cloudy and the polymer particle generated. Reaction mixed liquor was centrifuged and 150 ml of water washed precipitate particles twice.

[0047]To the precipitate particles which [silver complex support polymer particle prepared] washed, the mixed liquor of the silver nitrate 2.58g (0.0152 mol) and 150 ml of water is added, and it agitates at a room temperature for 2 hours, and is **. The silver complex support polymer particle (mean particle diameter of about 90-120 nm) was obtained by centrifuging mixed liquor, washing precipitate particles twice and carrying out reduced pressure drying with 150 ml of methanol (the yield of 8.6 g (dry solid conversion), 13.3 % of the weight of moisture contents, 35.2 % of the weight of silver content).

[0048]Example 3 [preparation of bridge construction hydrophilic polymer particles] acrylamide 4.5g (0.063 mol), The mixed liquor of the methylenebis acrylamide 2.4g (0.0156 mol) and the acrylic acid 1.1g (0.0152 mol), It added to 86 ml of ethanol, and the mixed solvent of 6 ml of water, and the precipitate polymerization was carried out at the temperature of 60 ** among argon atmosphere for 17 hours using 0.05 g of azobisisobutyronitrile. In this reaction, after heating in temperature of 60 **, after about 0.5-hour progress, the polymerization system became cloudy and the polymer particle generated. Reaction mixed liquor was centrifuged and 150 ml of water washed precipitate particles twice.

[0049]To the precipitate particles which [silver complex support polymer particle prepared] washed, the mixed liquor of the silver nitrate 2.58g (0.0152 mol) and 150 ml of water is added, and it agitates at a room temperature for 2 hours, and is **. The silver complex support polymer particle (mean particle diameter of about 90-120 nm) was obtained by centrifuging mixed liquor, washing precipitate particles twice and carrying out reduced pressure drying with 150 ml of methanol (the yield of 11.5 g (dry solid conversion), 13.9 % of the weight of moisture contents, 25.7 % of the weight of silver content).

[0050][Antibacterial evaluation] According to the Japanese Society of Chemotherapy standard method, the minimum growth alienation concentration (Media Interface Connector, ppm) estimated antibacterial properties as follows.

(1) silver silica gel system antimicrobial agent (about 3 % of the weight of the amounts of silver ions) of silver complex support polymer particle comparative example 1:marketing obtained in sample examples 1-3

Comparative example 2: A commercial silver zeolite system antimicrobial agent (about 3 % of the weight of the amounts of silver ions)

(2) use strain Staphylococcus: -- Staphylococcus . Aureus (Staphylococcus aureus) 209P JC-1 Escherichia coli: ESHIRISHIA The bouillon culture medium for Cori (Escherichia coli) NIHJ JC-2

(3) culture-medium susceptibility measurement and the agar

medium for sensitivity discs were used.
(4) Since test-method each sample was insolubility, it was suspended to purified water and the suspension of the 10 time concentration of examination concentration was prepared. When examining, it mixed and used at a rate of examination suspension 1 part by volume to culture-medium 9 part by volume. On the other hand, after cultivating one nights of test organisms at 37 ** using a susceptibility bouillon culture medium, it diluted with the culture medium suitably, and 10^6 cfu/ml test organism liquid was prepared. A result is shown in Table 1.
[0051]
[Table 1]

表 1

菌株	最小発育阻止濃度（MIC, ppm）				
	実施例1	実施例2	実施例3	比較例1	比較例2
S. aureus	1000	250	2000	>8000	4000
E. coli	500	250	2000	>8000	4000

In the antimicrobial polymer particle of Examples 1-3, high antibacterial properties are revealed compared with a commercial item so that clearly from Table 1.
[0052]Silver complex support polymer particle 1 weight section obtained in example 4 Example 2 and ultraviolet curing type paint (Toagosei make, ARONIKKUSU UV-3701) 99 weight section are mixed, The obtained dispersion mixing liquid was applied to the polyethylene terephthalate film by the bar coating machine, and the hardening layer was formed by irradiating with ultraviolet rays for 10 minutes using a high-pressure mercury lamp.
It replaced with the silver complex support polymer particle of comparative example 3 Example 2, and the hardening layer was formed like the above except using the antimicrobial agent of the comparative example 2.
[0053]Silver complex support polymer particle 1 weight section obtained in example 5 Example 2 and aqueous emulsion coating material (Toagosei make, Aaron NS-1200) 99 weight section (solid content conversion) are mixed, The obtained dispersion mixing liquid was applied to the polyethylene terephthalate film by the bar coating machine, it dried at the room temperature, and the coating film was formed.
It replaced with the silver complex support polymer particle of comparative example 4 Example 2, and the coating film was formed like the above except using the antimicrobial agent of the comparative example 2.
[0054]And the antibacterial properties of the coat film to said strain were investigated as follows. Staphylococcus. (Staphylococcus .)

After cultivating aureus (Staphylococcus aureus) 209P JC-1 and 37 ** of Escherichia coli (ESHIRISHIA Cori (Escherichia coli) NIHJ JC-2) by a nutrient broth culture medium (NB, Nutrition research) for 18 to 20 hours, It diluted with the nutrient broth culture medium (NB, Nutrition research) diluted to the concentration 1/500 suitably, and 10^5 cfu/ml test organism liquid was prepared. Put 1 ml of test organism liquid into an eye TSUKIN plastic petri dish (Sumilon) 35 mm in diameter, turn the film surface of the above-mentioned sample coat down, and test organism liquid was made to contact, after lower, the seal of the lid was carried out to the petri dish, and it was allowed to stand at the room temperature (25 **) on it for 24 hours. It was operated like the above, using (no processing) only in fungus liquid as contrast. The number of microorganism at the time of a start and the number of microorganism after 24-hour progress were measured by ****** using a nutrient agar medium (NA, Nutrition research), and change of the number of microorganism estimated the germicidal action. The antibacterial properties of a coat are shown in Table 2.

[0055]

[Table 2]

表 2

	菌株の種類	接触時間	
		0 h	24 h
実施例4	S. aureus	4.3×10^5	< 10
比較例3		4.3×10^5	1.5×10^5
実施例5		4.3×10^5	<10
比較例4		4.3×10^5	3.8×10^5
対照(無処理)		4.3×10^5	7.7×10^5
実施例4	E. coli	1.7×10^5	<10
比較例3		1.7×10^5	1.1×10^6
実施例5		1.7×10^5	< 10
比較例4		1.7×10^5	3.5×10^5
対照(無処理)		1.7×10^5	1.5×10^7

In the antimicrobial polymer particle of an example, high antibacterial properties are revealed compared with a commercial item so that clearly from Table 2. The hardening layer formed in Example 4 was a high hardening layer of transparency except having colored it yellow a little. On the other hand, the hardening layer formed by the comparative example 3 was colored reddish brown, and transparency also fell. Thus, in the antimicrobial

polymer particle of Example 2, probably because a silver ion exists as a complex, it is stable to ultraviolet rays. Particle diameter is dramatically small, since particles are moreover formed with the organic high polymer, the antimicrobial polymer particle of Example 2 does not have a difference of a refractive index with base resin (ultraviolet curing type resin), and its transparency is high. On the other hand, since the antimicrobial agent of the comparative example 2 has the small stability of a silver ion, coloring arises, and since it is as large as the particle diameter of about 1-3 micrometers and the difference of a refractive index with base resin is moreover also large, transparency is falling.

[Translation done.]